

UDC 546.05:617:666.3

COMPOSITES FROM MIXTURES OF POTASSIUM POLYTITANATE AND BIOCOMPATIBLE GLASSES

A. V. Gorokhovskiy,^{1,3} D. A. Cortes-Hernandez,² and N. N. Shcherbakova¹

Translated from *Steklo i Keramika*, No. 11, pp. 27 – 29, November, 2010.

The possibility of synthesizing ceramic composites from mixtures of powders of two types of biocompatible glass and potassium polytitanate was investigated. It was shown that during the reaction of these composites with a solution simulating blood plasma, a porous structure reinforced with potassium hexatitanate or calcium titanate fibers formed on the surface of the material; the pores were filled with hydroxyapatite, which should cause intergrowth of bone tissue in the structure of the implants made from them.

Key words: biocompatible glasses, potassium polytitanate, bioceramics, hydroxyapatite.

Calcium orthophosphates in the form of finely crystalline nonstoichiometric Na-, Mg-, and carbonate-containing hydroxyapatite, so-called biological apatite, are the basic inorganic component of solid tissues in the bodies of mammals. In addition to the calcium orthophosphates that constitute (by weight) 50 – 60% of bone, the other basic components of bone are collagens (30 – 40%) and water (up to 10%). Different types of bioceramics have been obtained by inorganic synthesis. The high affinity with bone tissue and the biodegradability with subsequent replacement by newly formed bone are considered to be the advantage of Cerasorb bioceramic made of $\text{Ca}_3(\text{PO}_4)_2$ (calcium orthophosphate) and $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ (hydroxyapatite) over other synthetic materials. Calcium orthophosphates in bioceramics belong to the category of bioactive and bioresorbable materials. Dissolved, they cause formation of a layer of biological apatite which results in the appearance of chemical bonds between implant and living bone and fusion to the bones, and these implants can bear mechanical loads [1]. The creation of a bioceramic with a porous structure with mechanical characteristics similar to those of living bone is important. For this reason, bioceramics began to be made macroporous (pore size greater than 100 μm) by adding blowing agents which are either volatile or readily soluble compounds (for example, naphthalene, saccharose, NaHCO_3 , NaCl , gelatin, polymethyl methacrylate microbeads) [2]. The implant must be hydrophilic and have a biodegradation rate corresponding to

the rate of formation of new bone — from several months to two years.

The properties of bioceramics are being improved in several directions — synthesis of ion-substituted calcium orthophosphates, creation of nanocrystalline structures, organo-mineral hybrids, ceramic fibers, microbeads, porous three-dimensional structures from hydroxyapatite and two-phase calcium phosphate, and bioceramics with a porosity gradient. Synthesis of composites simulating the composition and properties of bone tissue is being supported, and the study of nanostructured and nanocrystalline materials made of calcium orthophosphates to simulate the complex hierarchical structure of bones and teeth is expanding.

The composites are usually mixtures of several different components: an inorganic substrate containing elements of bone tissue growth factor or organic matrices with inorganic additives. Such materials as Kolapol, Hapcol, Biomatrix, etc., were created from hydroxyapatite and collagen.

The use of computer modeling of composites and many experimental studies have shown that the structure and properties, size and shape of filler particles, and the character of their reaction with the matrix are the factors that determine the increase in the mechanical strength and crack resistance of the synthesized material [3].

Selection of the biological material that ensures effective regeneration of bone tissue should be based on the results of experimental tests in the conditions of the biological medium.

A common characteristic property of all bioactive implants used in traumatology and orthopedics is the formation of a carbonate hydroxyapatite (CHA) layer on their surface on implantation. Equivalent to the mineral phase of bone in

¹ Saratov State Technical University, Saratov, Russia.

² Center for Scientific Research and Advanced Studies – CINVESTAV, Saltillo, Mexico.

³ E-mail: algo54@mail.ru.

TABLE 1. Calculated Composition of Components of the Initial Materials for Fabricating Composites

Raw material	Mass content of oxides, %					
	SiO ₂	Na ₂ O	CaO	P ₂ O ₅	TiO ₂	K ₂ O
PPT	0.5	—	—	—	81.3	19.2
Glass G1	46.1	22.0	26.9	5.0	—	—
Glass G2	30.4	—	49.7	19.9	—	—

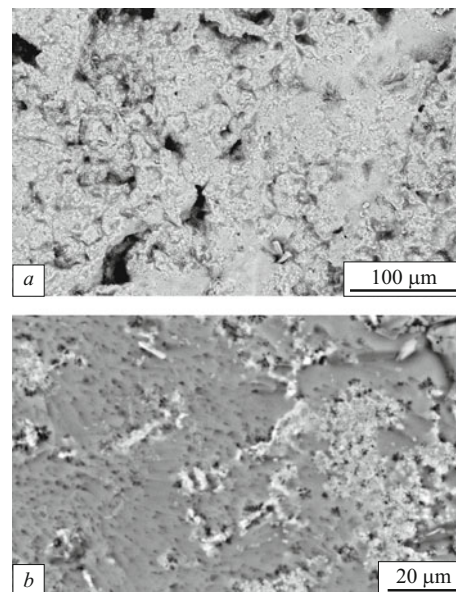
composition and structure, the CHA layer grows in the form of polycrystalline agglomerates containing collagen fibrils, so that the inorganic surface of the implant binds with the organic components of the tissues. The interface between bioactive implant and bone is almost identical to the naturally arising interfaces between bones, tendons, and ligaments. The mechanical properties of the biomaterial most completely correspond to natural stress gradients [4]. In order to give the implant the necessary properties, it is necessary to create materials with controllable resorption, and this is attained by using a bioactive component — hydroxyapatite and a mineral filler, which give the material the required mechanical and structural properties. There are biomaterials [5] obtained from hydroxyapatite and the natural mineral wollastonite and diopside, which can create a reinforcing network of diopside or wollastonite crystals in the implant; however, the increase in the strength in these materials is accompanied by an increase in the density (decrease in the porosity).

We conducted studies to obtain a new type of biocompatible material in the form of a glass ceramic composite in which the glass matrix is reinforced with crystalline fibers formed during reactive firing in sintering of the bioceramic. The results of previous studies [6, 7], where it was shown that fibrous calcium titanate and potassium hexatitanate crystals are high-strength biocompatible materials capable of fixing implant compounds with living bone, were the grounds for conducting this research. In addition, previously published studies [8] showed that high-strength crystalline potassium hexatitanate fibers are formed in heat treatment of amorphous potassium polytitanates during their combined firing with amorphous silica.

Two previously approved glass compositions represented in [9, 10] as satisfying the requirements for biocompatible materials were selected as the glass matrix for synthesizing the composite.

Potassium polytitanate (PPT) with $\text{TiO}_2/\text{K}_2\text{O} = 5.3$ prepared by the method described in [11] was selected as the precursor for creating the crystalline phase. The calculated compositions of the glass and potassium polytitanate are reported in Table 1.

A batch based on traditional materials: quartz sand, calcium carbonate (chalk), soda (sodium carbonate), ammonium hydrophosphate, was used for founding the biocompa-

**Fig. 1.** Structure of the composite of composition 1: *a*) initial (magnification $\times 300$); *b*) after holding in physiological solution for 5 days (magnification $\times 1000$).

tible glasses. The glass batch was founded in an electric furnace in different conditions:

glass G1 — the crucible with the batch was placed in a heated furnace at 1400°C and held for 2 h, then the glass melt was poured off into water;

glass G2 — the crucible was placed in a cold furnace, heated at the rate of 7 K/min to 1450°C , and poured off into water.

The glass granulate was ground to a powder in a ball mill. The mixture of the 0.1 – 0.35 μm fractions of the glass powder and PPT in the weight ratio of 50/50 was then ground in a ball mill for 30 min, and then blanks — pellets 1 cm high and 1 cm in diameter — were prepared by semidry molding with addition of an aqueous emulsion of dextrin under pressure of 24 MPa. The pellets were fired in an electric furnace at the maximum temperature of 1100°C .

The samples of the ceramic composites obtained: composite 1 with glass G1 and composite 2 with glass G2, were then tested for compressive strength.

The samples of the composites were exposed to physiological solution to determine the degree of biocompatibility. The concentration of ions in the solution was (mM): 142.0 Na; 5.0 K; 2.5 Ca; 1.5 Mg; 27.0 HCO_3 ; 1.0 HPO_4 ; 0.5 SO_4 [12].

The samples were investigated for new growths. The structure and phase composition of the ceramic samples obtained were investigated with electron-probe methods of analysis using a Philips XL30ESEM scanning electron microscope equipped with an EDAX Pegasus for local x-ray microanalysis. The photomicrographs of the composites obtained are shown in Figs. 1 and 2.

The photomicrographs obtained clearly show that composite 1 appears to be more similar to bone tissue with a

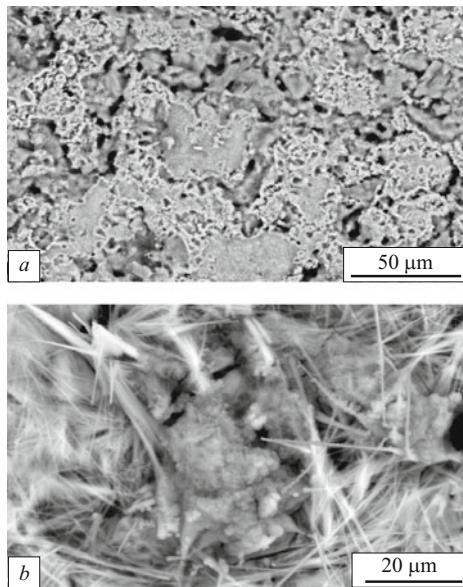


Fig. 2. Structure of the composite of composition 2: *a*) initial (magnification $\times 600$); *b*) after holding in physiological solution for 5 days (magnification $\times 1300$).

dense matrix and pores of different sizes than the sample of composite 2 (see Fig. 1*a* and Fig. 2*a*). An incrustation of new growth that coats the surface of the glass matrix is visible in Fig. 1*b*.

However, dissolution of the glass matrix of the material, baring the potassium hexatitanate and calcium titanate fibers and forming cemented hydroxyapatite structures between the fibers, confirmed by the data from local x-ray microanalysis, are seen in Fig. 2*b*, which shows composite 2 after holding in physiological solution for 5 days. The composition of the incrustation confirms the reaction: the calcium passes from the physiological solution into the hydroxyapatite, and the material remains monolithic with formation of the incrustation.

As the chemical analysis of the incrustation formed in the material after 3 days of testing with physiological solution showed, the ratio of calcium and phosphorus oxides (26.5/17.0) corresponds to the oxide content in hydroxyapatite (based on its chemical formula). According to the results of the analysis of the new growths in composite 2, fibrous crystalline phases are present together with hydroxyapatite: potassium hexatitanate $K_2TiO_6O_{13}$ and calcium titanate $CaTiO_3$. Composite 2 has almost 3 times higher mechanical compressive strength than composite 1, 11.4 and 4.1 MPa, respectively.

As a result of sintering the mixed biocompatible glass and potassium polytitanate powders, ceramic composites that react with physiological solution with formation of hydroxyapatite were obtained. The studies revealed the advantages of the composite of composition 2, since a fibrous reinforcing structure formed by potassium hexatitanate and calcium titanate fibers distributed in the glass matrix is formed. As a

result of exposure to physiological solution, the glass matrix dissolves, while the fibers are cemented by the new hydroxyapatite formations; because of this, the material has uniformly distributed porosity which is totally permeable to physiological fluids. Since the porosity is not formed by channels, but by the entire interfiber space, the pores are a continuous phase creating space for new growth and ligaments with living bone (tissue).

REFERENCES

1. V. I. Putlyaev and T. V. Safronova, "The new generation of calcium phosphate biomaterials: the role of phase and chemical compositions," *Steklo Keram.*, No. 3, 30 – 33 (2006); V. I. Putlyaev and T. V. Safronova, "A new generation of calcium phosphate biomaterials: the role of phase and chemical compositions," *Glass Ceram.*, **63**(3 – 4), 99 – 102 (2006).
2. R. Z. LeGeros and J. P. LeGeros, "Calcium phosphate bioceramics: Past, present, and future," *Key Eng. Mater.*, **240**(242), 3 – 10 (2003).
3. V. P. Tarasovskii, E. S. Lukin, and A. V. Belyakov, "Effect of crystal size on the microstructure and properties of ceramics," *Ogneupory*, No. 8, 11 – 14 (1991).
4. S. F. Hulbert, L. L. Hench, D. Forbers, and L. S. Bowman, "History of bioceramics," *Ceram. Intern.*, **8**(4), 131 – 140 (1982).
5. V. V. Shumkova, V. M. Pogrebenkov, A. V. Karlov, et al., "Hydroxyapatite–wollastonite bioceramics," *Steklo Keram.*, No. 10, 18 – 21 (2000); V. V. Shumkova, V. M. Pogrebenkov, A. V. Karlov, et al., "Hydroxyapatite–wollastonite bioceramics," *Glass Ceram.*, **57**(9 – 10), 350 – 353 (2000).
6. M. Kitano, K. Nakajima, J. Kondo, et al., "Protonated titanate nanotubes as solid acid catalyst," *J. Am. Chem. Soc.*, **132**(19), 6622 – 6623 (2010).
7. Ch. Cui, Y. M. Qi, M. F. Zhang, et al., "Histological and mechanical evaluation of the in vivo bone-bonding ability on the $K_2Ti_nO_{2n+1}/\beta$ -Ti alloy as a novel bioactive material," in: *Proc. Mat. Res. Soc., Paper # 1187-KK09-06* (2006).
8. M. A. Aguilar González, A. Gorokhovskiy, A. Aguilar Elquezabal, and J. I. Escalante García, "Síntesis y caracterización de adsorbentes cerámicos basados en polititanatos de potasio y vidrio $SiO_2 - B_2O_3 - R_2O - Al_2O_3$," *Bol. Soc. Esp. Ceram.*, **47**(1), 29 – 34 (2008).
9. P. D. Sarkisov, N. Yu. Mikhailenko, and Ts. M. Khavala, "Biological activity of glass and sital materials," *Steklo Keram.*, Nos. 9 – 10, 5 – 11 (1993); P. D. Sarkisov, N. Yu. Mikhailenko, and V. M. Havala, "Bioresistivity of glass and glass-ceramic materials," *Glass Ceram.*, Nos. 9 – 10, 5 – 11 (1993).
10. P. N. de Aza, A. H. Gutian, and S. de Aza, "Bioeutectic: a new ceramic material for human bone replacement," *Biomaterials*, Nos. 18 – 19, 1285 – 1291 (1997).
11. A. V. Gorokhovskiy, J. I. Escalante-García, T. Sánchez-Monjarás, and C. A. Gutiérrez-Chavarría, "Synthesis of potassium polytitanate precursors by treatment of TiO_2 with molten mixtures of KNO_3 and KOH ," *J. Eur. Ceram. Soc.*, **24**(13), 3541 – 3546 (2004).
12. K. Ono, T. Yamamuro, T. Nakamura, and T. Kokubo, "Quantitative study on osteoconduction of apatite–wollastonite-containing glass-ceramic granules, hydroxyapatite granules, and alumina granules," *Biomaterials*, No. 20, 2287 – 2303 (1999).